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Magnetic Clusters on Single-Walled Carbon Nanotubes: The Kondo Effect in a One-Dimensional Host

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Single-walled carbon nanotubes are ideal systems for investigating fundamental properties and applications of one-dimensional electronic systems. The interaction of magnetic impurities with electrons confined in one dimension has been studied by spatially resolving the local electronic density of states of small cobalt clusters on metallic single-walled nanotubes with a low-temperature scanning tunneling microscope. Spectroscopic measurements performed on and near these clusters exhibit a narrow peak near the Fermi level that has been identified as a Kondo resonance. Using the scanning tunneling microscope to fabricate ultrasmall magnetic nanostructures consisting of small cobalt clusters on short nanotube pieces, spectroscopic studies of this quantum box structure exhibited features characteristic of the bulk Kondo resonance, but also new features due to finite size.

Single-walled carbon nanotubes (SWNTs) exhibit unique electronic properties that have been the focus of considerable fundamental and applied research (1–3). Scanning tunneling microscopy (STM) studies have illuminated the fact that SWNTs can exhibit metallic or semiconducting behavior depending on diameter and helicity (3–5) and have confirmed the distinct van Hove singularities characteristic of one-dimensional (1D) systems (6). In addition, electrical transport measurements have shown that SWNTs can behave as low-temperature single-electron transistors (7, 8) and room-temperature field-effect transistors (9, 10), and can exhibit power-law behavior characteristic of a strongly interacting Tomonaga-Luttinger liquid (11, 12). These latter observations of strong electron-electron interactions, and our interests in understanding the response of SWNTs to local perturbations, has led us to investigate how magnetic atoms and clusters interact with SWNTs.

The interaction between the magnetic moment of a magnetic impurity atom and the conduction electron spins of a nonmagnetic host, termed the Kondo effect, is a well-known phenomenon that leads to anomalous transport measurements in bulk systems of dilute magnetic alloys (13). For temperatures below the Kondo temperature (T_K), electrons of the host screen the local spin of the impurity, resulting in the emergence of a Kondo resonance. This resonance should disappear at temperatures above T_K . A magnetic nanostructure composed of a magnetic impurity and a carbon nanotube host is an interesting

system because the impurity spins would interact with conduction electrons confined to 1D, and, in addition, might potentially spin-couple to a strongly (versus weakly) interacting electron system. The possibility of a Kondo state in SWNTs was recently suggested on the basis of thermopower measurements made on SWNT mats (14), although the complexity of such samples makes detailed analysis difficult.

We report spatially resolved STM measurements of the local electronic structure of magnetic cobalt (Co) clusters on metallic SWNTs. Recent STM investigations of magnetic atoms and clusters on noble metal surfaces show that local probes can provide unique insight into the Kondo problem by spatially characterizing the electronic density of states (DOS) in the vicinity of a magnetic center (15–17). These studies found narrow features in the tunneling spectra near the Fermi energy (E_F) above magnetic centers, which were identified as Kondo resonances. In addition, the structure in the resonances was attributed to quantum interference between the localized metal d or f orbitals and conduction electron channels (15–18). In the present study of SWNTs, an electronic resonance peak near E_F is observed in the spectra measured above the center of small Co clusters, and this resonance feature disappears over a distance of 2 nm from the cluster. Spatially resolved spectroscopy measurements made on small Co clusters on semiconducting SWNTs and nonmagnetic Ag clusters on metallic SWNTs show no evidence for this resonance, thus confirming

its origin as a Kondo resonance. In addition, the interaction between magnetic clusters and a finite-sized SWNT host with discrete conduction electron states was characterized, and an enhanced conductance at E_F above the Co atom was found.

Our STM measurements were performed in a home-built, ultrahigh vacuum STM that was stabilized at temperatures of either 80 or 5 K. Current (I) versus voltage (V) were recorded directly and differentiated using published methods (5, 6). Cobalt metal was thermally evaporated onto SWNT samples in situ at low temperature (19). The SWNT samples were prepared by spin-coating suspensions of SWNTs in 1,2-dichloroethane onto Au(111) surfaces (3, 5). Before Co deposition, extensive STM imaging and spectroscopy measurements showed that both the SWNTs and Au(111) substrate were clean and cluster-free. However, after Co deposition, small clusters with diameters of ~1 nm were observed on the Au(111) surface and nanotubes. We attribute these new features to Co clusters (20). A representative image (Figure 1A) shows well-resolved atomic structure of the SWNTs and small, well-separated Co clusters positioned on individual SWNTs.

The 0.5 nm in diameter Co cluster in Figure 1A was studied spectroscopically at 5 K; data were obtained at the Co site and at a clean SWNT site displaced ~7 nm away from the Co (Figure 1B). The differential conductance (dI/dV) spectrum recorded at the site removed from the Co center is finite and nearly constant over the small bias range used in this mea-

surement, consistent with the nanotube being metallic. Data recorded over a larger energy range (21) and van Hove singularity analysis confirms that this SWNT is metallic. In contrast, the dI/dV spectrum taken directly above the Co center shows a strong resonance peak near E_F , $V=0$. This spectroscopic feature was observed above 10 different small Co clusters (<1 nm) situated on metallic nanotubes and is strongly suggestive of the presence of a Kondo resonance in the 1D SWNTs.

To further support this suggestion, we investigated the spatial extent of the local magnetic perturbations by measuring the position-dependent decay of the resonance near E_F . Spectroscopic data obtained for a 0.7-nm-wide Co cluster on an atomically resolved metallic SWNT (Figure 1C) are shown in Figure 1D. At the center of the Co site (● in Figure 1, C and D), the resonance feature exhibits a peak structure similar in shape but slightly broader than the peak in Figure 1B. The peak feature systematically decreases in amplitude in spectra recorded at increasing distances from the Co center; the sharp resonance disappears completely after ~2 nm. This decay length is similar, although slightly longer than reported for Co atoms on either Au(111) or Cu(111) surfaces (16, 17).

A number of control experiments have been carried out to verify that the prominent spectroscopic resonances are due to the interaction of the magnetic Co with the metallic SWNTs; that is, are indeed Kondo resonances. First, we repeated these measure-

ments with nonmagnetic Ag clusters on SWNTs. Similar to the protocol described above for Co deposition, a clean, cluster-free SWNT sample supported on Au(111) was first prepared and characterized prior to Ag deposition. Figure 1, E and F, depict an atomically resolved image of a small, isolated Ag cluster on a SWNT and the corresponding dI/dV data recorded above the Ag site and on the nanotube 2 nm away from the cluster. The spectroscopic results show that there is no peak feature near E_F because of the presence of the small Ag cluster. This result demonstrates unambiguously that the presence of the magnetic Co cluster is critical to observe the resonance, which is consistent with the Kondo model, and that the observed peak feature is not simply an enhancement in the DOS due to a metal cluster. Second, spectroscopic measurements performed above Co clusters supported by intrinsic semiconducting SWNTs exhibited no features at E_F . This observation suggests that the peak feature at E_F is not due to the bare Co d -orbital resonance and emphasizes the necessity of conduction electrons in the host needed to interact with the magnetic cluster in order to observe the Kondo resonance.

To interpret the tunneling spectroscopy of small Co clusters on the nanotubes, we follow the theoretical model of (16) that considers the Anderson picture of a magnetic impurity in a nonmagnetic host (22). Within the framework of this model, a Co atom on a nanotube can be described as a discrete d -or-

bital in resonance with the continuum of the nanotube's conduction band states. The d -orbital spreads into a relatively broad d resonance that lies below the Fermi level, E_F ; for temperatures below T_K , some of the d -orbital density is shifted to E_F , forming a nearly Lorentzian resonance (23), the Kondo resonance. Similar to previous STM experiments of magnetic impurities on noble metal surfaces (15–17), in our experiment, two different paths are available for the electrons to tunnel from an STM tip: to the d -orbital of the Co magnetic impurity and to the continuous states of the nanotube. Because the final state of the electron can occupy two energetically degenerate possible states, this can lead to quantum interference. Fano's model of interference between a noninteracting discrete channel and a continuum may be expressed in terms of the rate of transition to a final state of energy ϵ (24)

$$R(\epsilon) \propto \frac{(\tilde{\epsilon} + q)^2}{\tilde{\epsilon}^2 + 1} \quad (1)$$

where $\tilde{\epsilon} = (\epsilon - \epsilon_0)/(\Gamma/2)$ is the dimensionless energy parameter detuned from resonance, ϵ_0 is the resonance energy, Γ is the width of the d resonance, and q is the interference parameter. The magnitude of q is proportional to the ratio of the matrix elements between the initial state to the discrete and continuum parts of the final state. In accordance with the theoretical results of (16), which includes an interacting resonant level, near the Kondo resonance ($T < T_K$)

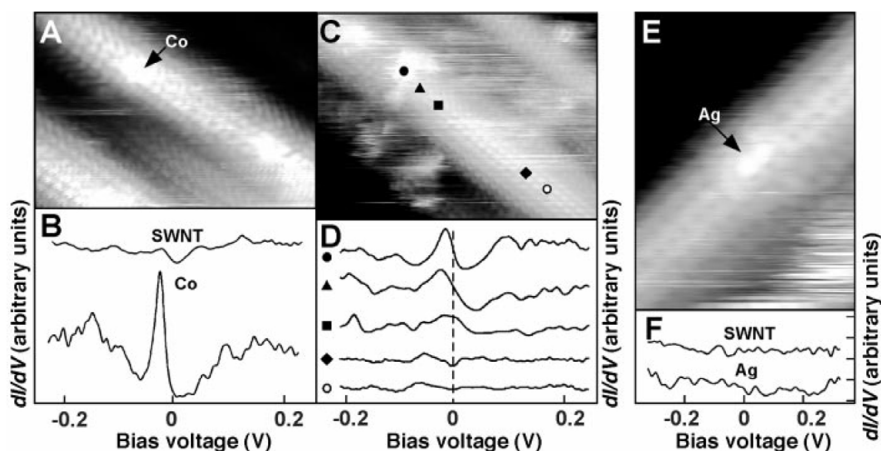


Figure 1. STM topographic images and spectroscopic measurements on small clusters situated on SWNTs. (A) Atomically resolved image of 0.5-nm Co clusters on an individual nanotube. (B) Differential conductance dI/dV versus V , calculated from I - V curves taken over the bare nanotube ~7 nm away from the Co and above the Co cluster in (A). The feature identified as a Kondo resonance appears above the Co. (C) Constant current image of slightly larger Co clusters (<1 nm in diameter) situated on resolved carbon nanotubes. (D) Differential conductance dI/dV as a function of position along the tube in (C) (indicated by the symbols ●, ▲, ■, ◆, and ○), starting with I - V performed above the cluster (●). The effect of the Co on the nanotube spectra is nearly gone after 2 nm. (E) Constant current image of a small Ag cluster on an individual nanotube. (F) Differential conductance dI/dV taken above the Ag cluster (Ag) and at bare nanotube 2 nm from the Ag (SWNT). The presence of the Ag cluster generates no spectroscopic peaks.

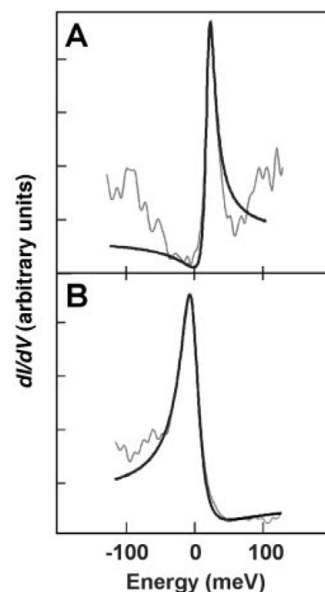


Figure 2. Spectroscopic measurements performed above Co clusters of different sizes and their fits to a modified Fano theory as described in the text. (A) A dI/dV spectrum of Co on SWNT shown in Figure 1A and its fit with parameters $q = -2.7$, $\alpha = -20$ meV, and $k_B T_K = 8$ meV. (B) A dI/dV spectrum of a slightly larger Co cluster on a SWNT with fit parameters $q = 3.3$, $\alpha = 8$ meV, and $k_B T_K = 16$ meV.

$$\tilde{\epsilon} = \frac{(\tilde{\epsilon} - \alpha)}{k_B T_K} \quad (2)$$

where α is a constant related to the shift of the resonance with respect to E_F and k_B is Boltzmann's constant.

We have quantified our results for small Co clusters on metallic carbon nanotubes by fitting the observed spectroscopic features using this model (25). The dark curve in Figure 2A shows a relatively good fit of Equations 1 and 2 to the data taken above the center of the Co center in Figure 1A (Figure 1B). The fit reveals that the Kondo temperature for Co/SWNT is ~ 90 K, confirming that the measurements at 5 K were made in the $T < T_K$ limit. To examine the validity of this prediction for T_K , we repeated our measurements at 80 K. Significantly, we found no peaks in dI/dV above Co sites situated on metallic SWNTs. We believe that this observation is consistent with the predicted value of T_K , although the disappearance occurs at a temperature ~ 10 K lower than that obtained from the fit. Interestingly, the Kondo temperature determined from our local spectroscopic measurement falls within the Kondo temperature range suggested on the basis of thermopower measurements on mats of SWNTs containing transition metal catalysts (14). In addition, we find that spectra taken above Co clusters of different sizes exhibit slightly different peak widths. Figure 2B shows the fit to a spectrum taken above a cluster whose diameter is 0.7 nm. In general, the larger clusters show broader peaks near E_F than do the smaller ones in the tunneling measurement (Figure 2A versus Figure 2B). This trend was also observed by previous STM investigations of Kondo impurities and can be explained within the Anderson model as an increased hybridization due to the overlap between neighboring magnetic atoms (15). However, in Co clusters with diameters > 1 nm, the net magnetic spin approaches that of a classical object, and as expected, the Kondo resonance disappears (26).

Magnetic impurities in 1D SWNTs also exhibit behavior that is quite distinct from that reported for 2D noble metal surfaces. The difference of d orbital localization of Co in its host is reflected in the line shape of the Kondo resonance, whose overall shape is governed by the magnitude of q . STM investigations of the Kondo effect on noble metal surfaces observed small values of q (0 to 0.7), which indicates that the transition probability from the STM tip to the localized d state is small compared with tunneling into the continuum; hence, the resonance is evident as a dip or antiresonance in the dI/dV . In our measurements of Co impurities on SWNTs, we obtained an estimate of the asymmetry parameter by fitting to the above model, and we found that $q = -2.7 \pm 0.5$ and

$q = 3.3 \pm 0.5$ for Co on the nanotubes (Figure 3, A and B). These large values of q lie in the range we found for all our clusters, $2 < |q| < 3.5$, which indicates that tunneling to the resonant state dominates over the continuum channel, and that the Kondo resonance exists as a peak near E_F . We speculate that this difference in tunneling probability to the Co d -orbital originates from the detailed characteristics of the nonmagnetic host, and may be due to differences between the delocalization of π -orbitals on carbon and those on noble metal surfaces or a reduction in the number of available final states in the 1D SWNT. Lastly, we comment briefly on the sign of q . Because of the quantum interference between the direct path and resonant path, each channel has a phase associated with it that depends sensitively on the details of how Co is coupled to the SWNT lattice. Hence, subtle changes in Co structure or cluster-surface coupling (27)

could readily lead to phase shifts and result in both positive and negative values of q . Experiments on smaller clusters and atoms whose position and spin can be registered with respect to the underlying lattice should resolve this point.

The ultimate magnetic nanostructure is perhaps a magnetic atom in a quantum box, where electrons are confined in all three dimensions and exhibit a discrete level spacing, ΔE . How the Kondo resonance may manifest itself in an environment where the energy-level spacing $\Delta E > T_K$ is an interesting question that has been addressed in recent theoretical studies (28). To attack this problem experimentally, we used the STM to "cut" the 1D nanotube into a SWNT quantum box. In shortened carbon nanotubes with length L , the electron energy-level spacing scales as $1/L$, and discrete levels are readily observed at 5 K (3, 29).

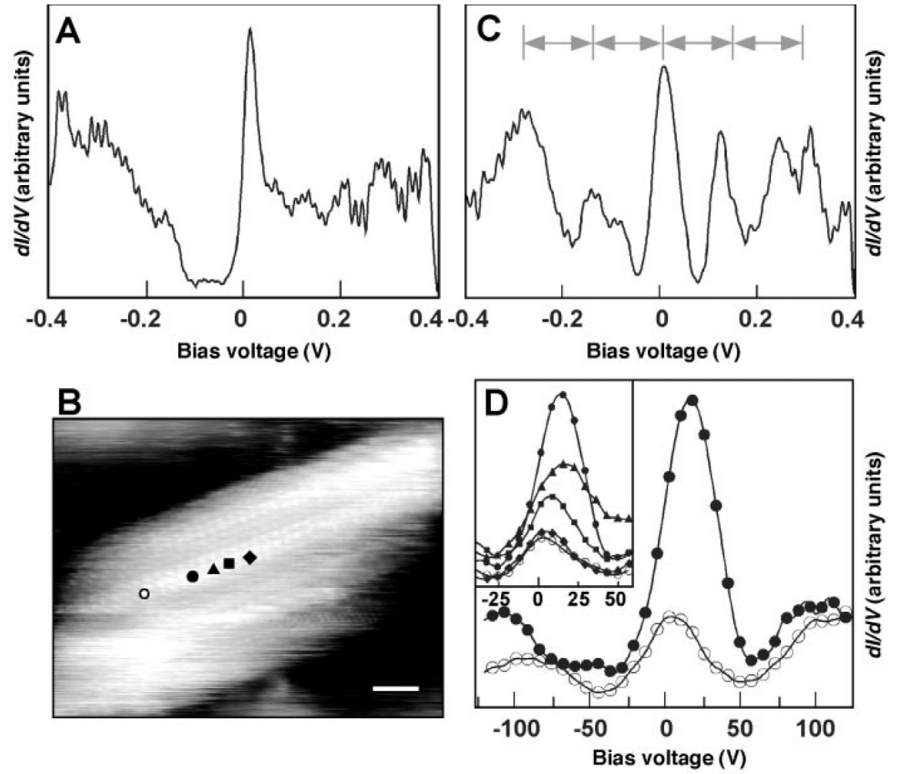


Figure 3. STM spectroscopic and topographic measurements. (A) Shown is a dI/dV spectrum recorded at the site of a small Co cluster on a long nanotube. This same tube and Co site was probed in the data presented in (B) through (D). (B) Atomically resolved image of a nanotube shortened to 11 nm. The symbols \bullet , \blacktriangle , \blacksquare , \blacklozenge , and \circ indicate the positions at which I - V curves were taken, and the filled black circle (\bullet) highlights the position of the cluster. Voltage pulses, typically 7 V and lasting 100 μ s, were applied between the STM tip and the nanotube on both sides of the Co cluster to create the nanotube segment. The scale bar corresponds to 1 nm. (C) Shown are dI/dV results obtained at the position of the small Co cluster in (B). The gray arrows indicate a near-equidistant peak-splitting characteristic of the discrete energy-level spacing of an 11-nm nanotube quantum box. (D) Comparison of the peak amplitude near E_F recorded at the Co cluster (\bullet) and ~ 1.5 nm away (\circ). (Inset) Shown are dI/dV data recorded at the positions indicated in (B). The amplitude of the central peak at E_F decreases systematically as spectra are recorded further and further from the Co center. The amplitude decay is similar in both directions (e.g., curves \circ and \blacklozenge).

We spectroscopically characterized Co on SWNTs before and after manipulating the nanotube length. The familiar Kondo resonance is observed near $V = 0$ in the dI/dV for spectra taken above a Co cluster situated on an uncut metallic SWNT (Figure 3A). An atomically resolved 11-nm nanotube segment created by applying voltage pulses on each side of the Co cluster is shown in Figure 3B. Spectroscopic data recorded above the Co site (Figure 3C) exhibit an average level spacing, indicated by gray arrows, of ~ 0.15 eV. This spacing agrees with expectations (3, 29), $\Delta E \sim 1.67$ eV/L ($= 11$ nm), and notably is an order of magnitude larger than the width of the Kondo resonance. The spectroscopic results recorded at the same position as the Co site are substantially different from the overall dI/dV structure observed in previous experiments on shortened metallic SWNTs (3): the peak amplitude at E_F appears markedly enhanced relative to the other energy-level peaks.

To investigate the origin of this increased conductance, we characterized the level structure near E_F versus distance from the cluster (Figure 3D). Interestingly, the amplitude of this central peak at E_F decreases over the same length scale, 2 nm, as the Kondo resonance decays from a Co cluster along an extended 1D SWNT, although the amplitude of peaks at $E \neq E_F$ is similar. The enhanced conductance at E_F provides evidence to how sensitive the electronic properties of metallic nanotubes are to magnetic impurities, even in finite-sized structures. Finally, it has been predicted that in confined electron systems where $\Delta E > T_K$, the Kondo resonance will be split into a series of subpeaks spaced by ΔE and will exhibit different features around E_F , depending on whether the total number of electrons in the box is odd or even (28). Within this framework, we can tentatively assign our finite-sized magnetic structure as an odd Kondo box, because a peak rather than a dip is observed at E_F . Studies using gated tips (30) could probe this assignment further by changing the number of electrons on the nanotube quantum box.

Overall, the present study indicates that many basic features of the Kondo effect are similar in 1D strongly interacting systems as they are in Fermi liquids. SWNT hosts of varying size provide much flexibility for investigating the Kondo effect at different energy scales. When this is combined with in-

vestigations of temperature and magnetic field, it could add much to our understanding of the Kondo resonance and how electron correlations in 1D modify the standard picture. We believe that STM will be critical to such studies, and moreover, may uncover unique applications of these nanostructures.

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19. The Co clusters were produced in ultra-high vacuum by resistively heating Co wire wrapped around a W filament with the sample held at ~ 100 K. The sample consisted of laser-ablated SWNTs supported on Au(111)/mica surfaces, prepared as in (3).
20. Average cluster sizes were less than 2 nm in width, and were typically 0.5 to 1 nm in diameter, containing about 3 to 30 atoms, respectively. Because atom diffusion along the sample surface leads to cluster formation, we estimate that a majority of the smaller clusters exhibit single- or double-atom heights.
21. T. W. Odom, J.-L. Huang, C.-L. Cheung, C. M. Lieber, data not shown.
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25. The Fano model assumes a single spin-1/2 atom within a free-electron host. The Co/SWNT system is more complicated than this for several reasons and deserves further theoretical treatment. First, the net spin in the clusters and the details of their ferromagnetic exchange coupling are unknown. Second, the precise nature of Co clusters coupling to the nanotube surface is not well defined. Finally, electron-electron correlations of the nanotube host may be important.
26. We find that small clusters with diameters between 0.5 to 0.8 nm (about 3 to 10 atoms) exhibit a Kondo resonance peak, while larger clusters with diameters > 1 nm (> 30 atoms) do not, and instead exhibit an energy-level spectrum characteristic of small Co nanoparticles, similar to spectra observed in transport measurements by S. Gueron *et al.* [*Phys. Rev. Lett.* **83**, 4148 (1999)].
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